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NASA TECHNICAL TRANSLATION

NASA TT F-14,720

THEORY OF SOLID COMPOSITE PROPERGOL COMBUSTION

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H.C. NTIS \$3.75

Translation of: "Theorie de la Combustion des Propergols
solides composites," Entropie No. 40, July-
August 1971, pp. 4-13

(NASA-TT-F-14720) THEORY OF SOLID
COMPOSITE PROPERGOL COMBUSTION M.
Bernard (NASA) Dec. 1972 33 p CSCL
21B 21B Unclas
G3/33 49514
N73-13955



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 DECEMBER 1972

THEORY OF SOLID COMPOSITE PROPERGOL COMBUSTION

Michel-Louis BERNARD

We present a theory of ammonium perchlorate propellant combustion, on the basis of a surface reaction as limiting process of the ablation rate. The adsorbed state of gaseous reagents, generated by pyrolysis, introduces the influence of pressure. Thus, we account for the role of pressure, composition, etc...

1 - INTRODUCTION

1.1. The combustion of solid propergols has been the subject of numerous projects, instigated by very old used of propellant powders. Among the various characteristics which define the conditions for use of these propergols, the combustion rate is one of the main ones. The combustion of a solid propergol is normally displaced on its surface in parallel layers (PIOBERT'S law). The rate of displacement of the emission surface of the gases, counted on the normal of this surface, is called the combustion rate of the powder or even the ablation rate or regression rate. This rate is generally inclusive between several millimeters and several centimeters per second. The sensitivity of powder combustion to pressure and initial temperature of the unit creates an inconvenience in their use. It is therefore important to know the laws as exactly as possible and, if possible, to understand the mechanics, if all or part of these inconveniences are to be remedied. This is

the reason why the pressure influence on the combustion rate of powders has held the attention of both theoreticians as well as researchers.

As VERDIER [1] reminds us, no single formula valid for all powders has until now been established, whatever the pressure.

The following various forms have been adopted depending on the type of powder and the pressure level considered, in the absence of gas circulation, parallel to the surface of the combustion block (erosive combustion):

$$V = C_p \quad (1)$$

$$V = V_o + C_p \quad (2)$$

$$V = C_p^n \quad (3)$$

$$V = V_o + C_p^n \quad (4)$$

Although the artillerymen prefer the linear law (2) called the MURAOUR law, the most frequently adopted in internal ballistics is the parabolic law (3) called the SAINT ROBERT law or VIEILLE law in which C is independent from p and n independent from T . The exponent n , generally between 0 and 1, inclusive, represents the sensitivity of the combustion to pressure. It should be selected at less than 1 so that the propellant combustion remains stable.

Part of this work has been the subject of a paper at the Evian Symposium of the French Physics Society, May 24-29, 1971

1.2. The propellant powders are classified into homogenous powders (colloidal powders, nitrocellulose base) and heterogenous powders [2]. The latter, also called composite powders, use an oxidizing mineral salt as a carburant which is introduced in a crytallized form and finely pulverized (nitrate or acaline perchlorate), dispersed at the center of a solid combustible forming the matrix (generally a polymer) which gives the powder its mechanical stability, as well as various additives, certain ones of which are intended to catalyze the combustion (copper chromite, for example).

The analysis of the physio-chemical processes of powder combustion with a view to accounting for their sensitivity to pressure has been the subject of a considerable number of projects. If, in the case of colloidal powders a schematic has been set up that has been generally accepted by different authors and has allowed calculation of the greatness of the experimental results, this is not the case for composite powders. For these, the combustion process is still not well understood, and no theory has yet allowed a complete explanation of the observed results. According to these theories [3], the control of combustion rate is localized in the gaseous phase in which the vapors coming to the surface deteriorate. The intensity of the heat flux transmitted from the gaseous phase to the surface thus determines the regression rate. These theories can, moreover, be classified into two categories depending on the type of flame used:

- Diffusional flame type theories, for which the heat disengagement in the gaseous phase is controlled by the diffusion rate of oxidizing gases and reducing agents one to the other. The most known of these theories is that of SUMMERFIELD [4]. For the regression rate V_B it leads to the following formula:

$$\frac{1}{v_B} = \frac{C_1}{p} + \frac{C_2}{p^{1/3}} \quad (5)$$

(C_1 and C_2 being two constants).

Elsewhere may be noted the HERMANCE model [5] derived from the preceding.

- Pre-mixed type flame theories, in which it is assumed that the gases emitted from the surface form a homogenous mixture and react (CHAIKEN model [6] for example).

- Other theories, such as that of NADAUD [7] which introduces the idea of "diffusional flame rate" depending on the size of the perchlorate granules, allow for the mixed characteristic of the flame.

- Besides heat transfer by diffusion toward the surface, certain authors have also allowed the possibility of transfer by radiation, for example BLAIR and coll. [8] in the form of a correction in the expression of rates calculated according to preceding theories.

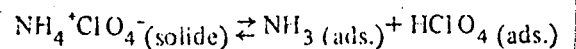
1.3. However, for several years, a certain amount of criticism

has been made on encountering these theories. For example, the CHAIKEN theory of pre-mixed flame only leads to a linear regression rate as a function of the pressure, a very restrictive formulation. As for flame diffusion theories, they have been criticized in particular by WENOGRAD and SHINNAR [9]. In fact, according to these authors, calculations show that the heat flux by flame diffusion toward the surface would be insufficient to assure the decomposition of ammonium perchlorate. Besides, given the weak concentration (0.5%) wherein the copper chromite acts as a catalyst, it is hardly probable that catalyzation in the gaseous phase would be possible. All of these remarks leading to placing the critical stage in the heterogenous reactions on the surface, have caused a certain number of researchers to be interested in the mechanics of the decomposition of the ammonium perchlorate and have proposed various schematics.

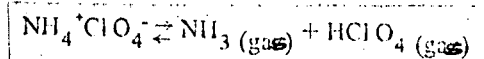
The ideas held are as follows:

- The reaction of the proton transfer seems to be the primary reaction of the decomposition (BOLDYREV and Coll.

[10]):



- The optical measurements of the surface temperature show that when the decomposition of the perchlorate occurs in the presence of the gaseous fuels or combustible binding agent, the monovariant equilibrium:



is well verified (POWLING and SMITH [11]).

- The perchloric acid would decompose according to a pattern that can be radical (JACOBS and PEARSON [12] or ionic ROSSER, INAMI and WISE [13]).

- The following stage would be the oxidation of the ammonia by a chlorine-oxygen compound coming from the decomposition of the perchloric acid HClO for JACOBS and PEARSON [12], ClO_3^+ for ROSSER, INAMI and WISE [13].

- According to certain authors, the catalyst reacts initially on the proton transfer reaction (JACOBS and RUSSEL [14] PITTMAN [15]). Its presence in the ammonium perchlorate would affect the equilibrium $\ln P = f(1/T)$ according to POWLING [16]. Various hypotheses can thus be made on the nature of the critical stage so that no proof need be supplied in favor of one of them. The mechanics proposed in the above-cited works nevertheless allow the choice of a decomposition of the perchloric acid adsorbed at the surface, for the critical stage. In fact, this choice shows the advantage of explaining the presence on the surface of oxidizing types capable of reacting on the adsorbed ammonia and on the fuel. A model can thus be developed on the basis of this hypothesis which explains at the same time the presence of the equilibrium at the surface mentioned by POWLING [16], the law of observed speed as well as the variation of the combustion rate as a

function of the pressure.

1.4. In order to approach the problem of the combustion of solid composite propergols, we were equally inspired by the results of research that we have carried out since 1963 on the combustion of hybrid propergols. (*) According to these results, the physio-chemical phenomena at the surface of the combustible solid (superficial chemical reaction coupled possibly with the mass transfer of reagents and products) limit the rate of combustion observed, both in the liquid-solid fuel mode and in the gas-solid mode.

The ablation of the solid fuel by the liquid or gas supporting combustion is thus expressed in a very general way as a function of the fluid flow rate (or better, the Reynolds number associated with it) and the pressure (figure 1).

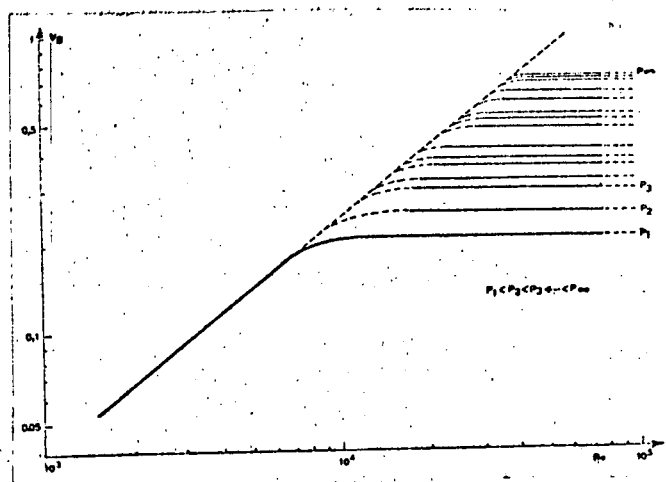


FIGURE 1 - Ablation rate as a function of the "Reynolds" number and of the pressure (hybrid combustion).

(*) Research carried out under research contracts from the Office of Research and Test Methods (D.R.M.E.) in conjunction with the National Office of Research and Aerospace Research (O.N.R.A.).

In a purely kinetic operation, the ablation rate (v_B) can be described as the rate of heterogenous attack of the solid fuel by the oxidizing agent adsorbed at the surface, the superficial concentration (θ_{ox}) of the latter being given by the LANGMUIR isotherm:

$$\theta_{ox} = \frac{(k_a/k_d) P_A}{1 + (k_a/k_d) P_A}$$

with: $P_A = kP$

whereby:

$$v_B = \frac{AP}{1 + BP} \quad (\text{fig. 2}).$$

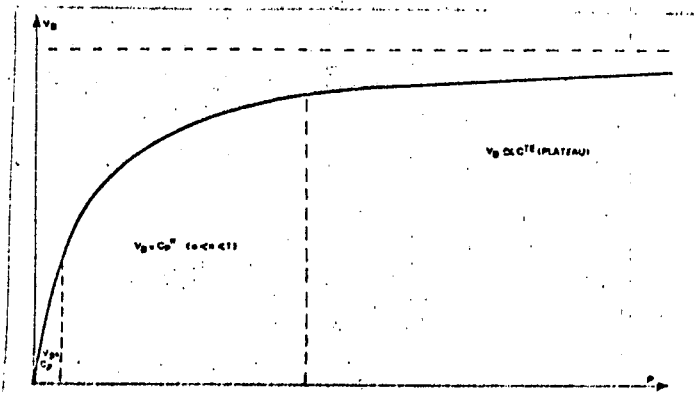


Figure 2 - Ablation rate as a function of the pressure in kinetic operation (hybrid combustion).

Account is also taken of the high pressures of a rate limit of hybrid combustions observed on propellers [17 and 18]. In this theory called the "Ablation Theory", the effect of heat transfer on the ablation is erased, at least in a purely kinetic operation, by the fact that the temperature at which the heterogenous reaction is carried out on the surface is imposed by a monovariant equilibrium, introducing a formula of the type $f(P, T)=0$. In the examples encountered in mybrid combustion, this monovariant equilibrium can correspond to the fuel fusion or to the vaporization of the supporting combustion

(case of liquid-solid ablation). But it is easy to imagine that this monovariant equilibrium can be introduced by the chemical transformation of a propergol compound (dissociative equilibrium for example).

2. COMBUSTION THEORY FOR AMMONIA PERCHLORATE BASE POWDERS

2.1. General Principles

The theory explained here is relative to the combustion of ammonia perchlorate and the associated composite powders, but its combustion principle is easily generalized for other perchlorates and nitrates. According to this theory the combustion rate (in the absence of gaseous current at the surface) is controlled by the rate of a heterogenous reaction at the surface of the ammonia perchlorate. The fundamental hypotheses are as follows:

- The ammonium perchlorate is in dissociative equilibrium in the reaction surface with its decomposition products, perchloric acid and ammonia.

- The "cool" gases in contact with the solid are made up of perchloric acid, ammonia and possibly other combustible molecules coming from either the decomposition of the binding agent or from the exterior (atmosphere reducing agent).

- Under the pressure and temperature conditions prevailing on the propergol surface certain types of "cool" gases are adsorbed in this surface depending on the distinct adsorption

sites.

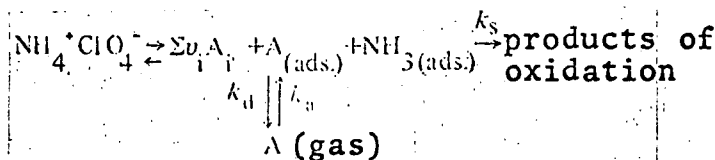


- The combustion rate of propergol is controlled by the rate of one or many oxidizing reactions in the adsorbed phase of the fuel types with perchloric acid.

2.2. Case of Pure Ammonium Perchlorate

In the case of pure ammonium perchlorate decomposition it is assumed that the limitative stage of rapidity is the reaction between the perchloric acid (A) and the ammonia at the adsorbed stage on the surface of the perchlorate crystals.

The mechanics of perchlorate decomposition can be shown in the following manner:



Let us write that the concentration of $\text{A}_{(\text{ads})}$ is stationary:

$$\frac{d(\text{A}_{\text{ads}})}{dt} = k_d \theta_A - k_a (1 - \theta_A) P_A + k_s \theta_A \theta_{\text{NH}_3} = 0$$

P_A being the partial pressure in active oxidizing agents (HClO_4) and θ_A and θ_{NH_3} being the respective recovery rates of oxidizing agents and ammonia sites. Given the strong adsorption of NH_3 on the perchlorate [19] we can make: $\theta_{\text{NH}_3} = 1$, from which

$$\theta_A = \frac{k_a P_A}{k_d + k_s + k_a P_A}$$

So, if we admit that the oxidation rate is slower (it limits the whole reaction) we can consider that the adsorption - desorption equilibrium type A is attained ($k_s \ll k_d + k_a P_A$).

That is, besides $S(\phi, \epsilon)$ the reaction surface which depends on the diameter ϕ of the perchlorate granules and the porosity ϵ of the powder, and S_0 the straight cross-section of the block, in writing, we have all oxidation of the produced ammonia by dissociative sublimation of the perchlorate is done in the adsorbed phase:

$$v_B = -\frac{1}{S_0} \frac{d^v \text{NH}_4 \text{ClO}_4}{dt} = -\frac{1}{S_0} \frac{d^v \text{NH}_3}{dt} = + \frac{S(\phi, \epsilon)}{S_0} \frac{M k_s k_a P_A}{\rho k_d + k_a P_A}$$

with: M the molar mass of ammonia perchlorate and ρ its volume mass.

In making the hypothesis that the active oxidizing type represents a constant fraction of the gas at the surface ("cool" gas) $P_A = kP$ with $K \ll 1/2$, P being the total pressure we have:

$$v_B = \frac{S(\phi, \epsilon)}{S_0} \frac{M}{\rho} k_s \frac{(k_a/k_d) kP}{1 + (k_a/k_d) kP} \quad (6)$$

The constants: k_a , k_d and k_s are linked to the surface temperature T_s by the equations:

$$\frac{k_a}{k_d} = \left(\frac{k_a^0}{k_d^0} \right) \exp\left(-\frac{E_A}{RT_s}\right) \text{ et } k_s = k_s^0 \exp\left(-\frac{E_s}{RT_s}\right)$$

with: E_A , adsorption energy of the oxidizing type and E_s , activation energy of the oxidation reaction of the ammonia.

In combustion at an initially imposed temperature, the homographic law represented by the equation (6) will be valid.

This is what was verified from the experiment results of WATT and PETERSEN (Figure 3).

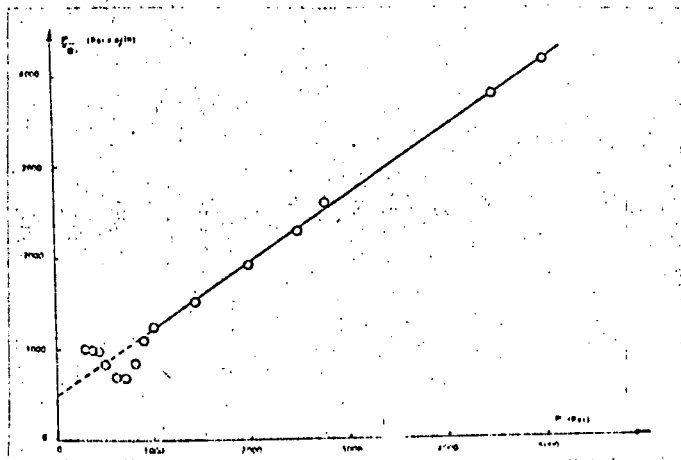


Figure 3 - Combustion of the pure ammonium perchlorate at a constant initial temperature, taken from experiment results of WATT and PETERSEN (ref. No. 20).

In free combustion, on the other hand, the surface temperature and pressure will not be independent variables because of the equilibrium of the dissociative sublimation, but will be connected by the expression of:

$$\ln(P/P_0) = A - B/T_s$$

The ablation rate will be written then, if we take for one unit of pressure $P_0 = 1$ bar,

$$v_B = + \frac{S(\phi, \epsilon)}{S_0} \frac{M}{\rho} k_s^0 \left(\frac{k_a^0}{k_d^0} \right) k \frac{P \left(1 + \frac{E_s - E_A}{RB} \right)}{1 + \left(\frac{k_a^0}{k_d^0} \right) k P \left(1 - \frac{E_A}{RB} \right)}$$

$$v_B = \frac{a P (1 + \alpha - \beta)}{1 + b P (1 - \beta)}$$

(7)

with:

$$a = \frac{S(\phi, \epsilon)}{S_0} \frac{M}{\rho} k_s^0 k \left(\frac{k_a^0}{k_d^0} \right), \quad b = k \left(\frac{k_a^0}{k_d^0} \right); \quad \alpha = \frac{E_s}{RB} \text{ et } \beta = \frac{E_A}{RB}$$

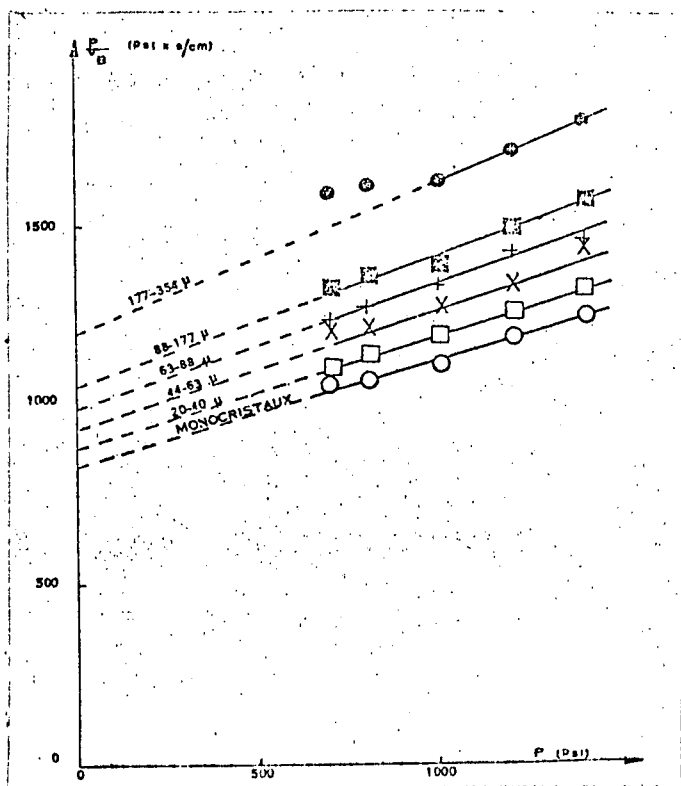


Figure 4 - Combustion of the pure ammonium perchlorate for different grain sizes, taken from experiment results of SHANNON and PETERSEN (ref. No. 21).

The values of α and β are generally small compared to the unit and we can make, more or less in a small pressure interval: $\alpha=\beta=0$. This is what can be verified from the experiment results of SHANNON and PETERSEN [21] (Figure 4) on various samples of perchlorate having various particle size distributions.

2.3. Case of Ammonia Perchlorate Base Propergols

2.3.1. Fundamental Equations

The preceding theory can be generalized in the case of propergols having a base of perchlorate and associated with a combustible binding agent by introducing:

- a new superficial reaction of the rate constant k'_s

- the partial pressure due to small molecule vapors f coming from the pyrolysis of binding agent F, depending on the reaction: $F_{\text{solid}} \rightarrow k f_{\text{gas}}$.

That is: x the molar fraction of the ammonia perchlorate in the powder, X its mass fraction, M_{PA} and M_F the molar masses of the ammonia perchlorate and the binding agent, we have $\frac{X}{1-X} = \frac{M_{PA}}{M_F} \frac{x}{1-x}$. The partial pressures being assumed proportional to the number of gasified moles, the statement of pressures in "cool" gases is established in the following manner:

$$\frac{P_{NH_3}}{x} = \frac{P_{HClO_4}}{x} = \frac{P_f}{(1-x)k} = \frac{P}{2x + k(1-x)}$$

that is:

$$P_{HClO_4} = \frac{P}{2 + k\left(\frac{1-x}{x}\right)} = \frac{P}{2 + k \frac{1-X}{X} k \frac{M_{PA}}{M_F}} = \frac{P}{K(X)}$$

The same as in the preceding case we will write that the critical stage rate is proportional to the recovery rate θ of the oxidizing type. We will thus have a new rate constant k'_s :

$$\frac{dv_{PA}}{dt} = -k'_s \cdot S(\phi, X) \cdot \frac{M_{PA}}{P_A} \cdot \theta,$$

$S(\phi, X)$ being the reaction surface, P_{PA} the volume mass of ammonium perchlorate and v_{PA} the volume of ammonium perchlorate in the powder. The linear regression rate v_B then becomes $v_B = v_B^* \cdot 0$

$$\dot{v}_B = \frac{1}{S_0} \left(\frac{d v_{PA} + v_F}{dt} \right) = \frac{1}{S_0} \left(\frac{\rho_{PA}}{\rho_F} \frac{1-X}{X} + 1 \right) \frac{d v_{PA}}{dt}$$

with: $\dot{v}_B^* = \frac{S(\phi, X)}{S_0} \left(\frac{\rho_{PA}}{\rho_F} \frac{1-X}{X} + 1 \right) \frac{M_{PA}}{\rho_{PA}} k'_s S_0$ being the straight

cross-section of the propergol.

If we make $P^* = \frac{k_d}{k_a}$, the adsorption-desorption equilibrium being attained, we have

$$\frac{P}{v_B} = \frac{P^*}{v_B^*(X, \phi)} [K(X) + \frac{P}{P^*}] \quad (8)$$

In fact, following the dissociative sublimation of the perchlorate [16] $K_P = P_{NH_3} \cdot P_{HClO_4} = \frac{P^2}{K^2(X)}$ and its surface

temperature T_s and pressure P , are linked by the expression

$$\ln P = A' - \frac{B'}{T_s}$$

making:

$$\begin{aligned} \frac{E'_s}{RB'} &= \alpha \quad \text{et} \quad \frac{E'_a}{RB'} = \beta \\ v_B^* &= v_B^{*0} \left(\frac{P}{\exp(A')} \right)^\alpha = v_B^{*0} \exp\left(\frac{E_s}{RT_s}\right) \\ P^* &= P^{*0} \left(\frac{P}{\exp(A')} \right)^\beta = P^{*0} \exp\left(\frac{E_a}{RT_s}\right) \end{aligned}$$

We obtain the general equation:

$$\frac{1}{v_B} = \frac{1}{v_B^{*0}} \left(\frac{P^{*0} \exp(A')^\alpha - \beta K(X)}{P^{1+\alpha} - \beta} + \frac{\exp(A')^\alpha}{P^\alpha} \right) \quad (9)$$

In the area of pressure where the critical stage has for a rate constant k'_s , we will have an equation of the type:

$$\frac{P^{1+\alpha} - \beta}{v_B} = D_1 + E_1 P^{1-\beta}$$

2.3.2. Verification

Bringing into Evidence, Operation at Low Pressure

As a first approximation of the preceding equation, we can have $\alpha=\beta=0$ which corresponds to the case of isothermic combustion or more or less at a limited combustion at a restrained pressure interval, as in the case of pure ammonium perchlorate. We have thus:

$$\frac{P}{V_B} = D_i + E_i P, \quad (10)$$

This expression is verified satisfactorily by the experiment results of TABACK [4] (Figure 5). The transformed illustration of this author in the area of low pressures (0 to 200psi) (Figure 6) also allows bringing out two distinct operations in propergol combustion and located here and there, having a pressure P' , between 80 and 160 psi inclusive. It is a phenomenon which will be made evident during this study.

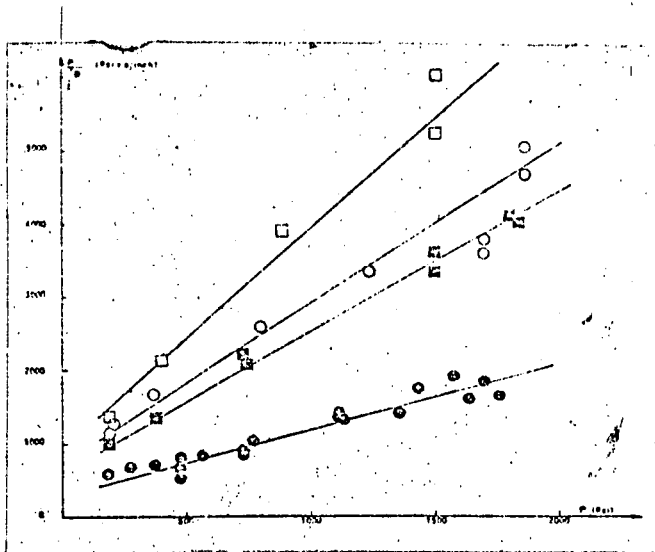


Figure 5 - High pressure combustion of an ammonium perchlorate base propergol (binding agent: polyester), taken from experiment results of TABACK (ref. No.4).

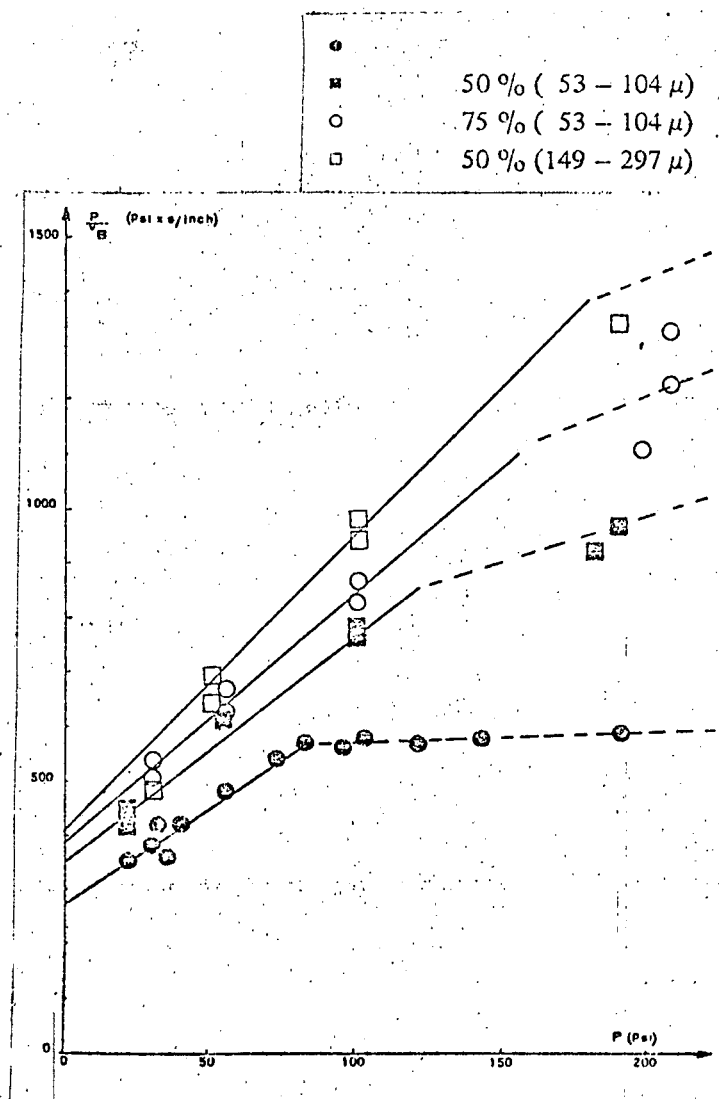


Figure 6 - Low pressure combustion of an ammonium perchlorate base propergol (combustible: polyester), taken from the experiment results of TABACK (ref. No. 4).

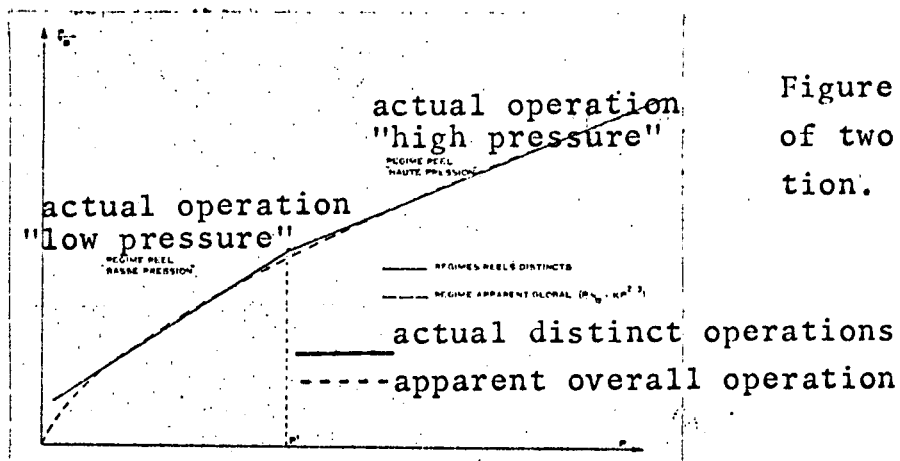


Figure 7 - Separation of two areas of combustion.

2.3.3. Significance of the SUMMERFIELD Formula and Area of Validity

If we make $\alpha=\beta=1/3$ the equation (8) becomes:

$$\frac{1}{v_B} = \frac{1}{v_B^0} K(X) \frac{P^*}{P} + \frac{\exp(A')^{1/3}}{P^{1/3}} \quad (11)$$

It is then identical to the SUMMERFIELD equation [4], an expression which would then correspond to a particular case of our theory for which:

$$E_a = E_s = \frac{RB'}{3} = \frac{1}{3} R \frac{\Delta H_{\text{subl.}}}{2R} = \frac{\Delta H_{\text{subl.}}}{6} = 10 \text{ Kcal/mole.}$$

It is noted nevertheless that the use of a formula such as that of SUMMERFIELD can lead (independently from any theoretical interpretation) to an erroneous understanding of the experimental results, and witness to this fact is, the analysis that SUMMERFIELD made of TABACK'S results[4].

In fact this representation in $P^{2/3}$ (equation 11) having a tendency to interpolate using a parabol of successive linear representations, the existence of a distinct low pressure rating escaped him (Figure 7).

2.3.4. Combustion of Ammonium Perchlorate in Gaseous Fuels

When the free combustion of the ammonia perchlorate is no longer maintained on this side of pressure P , generally around 20 bars, its combustion in various gaseous fuels is automatically maintained at a much lower pressure. By using

the simplified representation $\frac{P}{v_B}$, P (equation 10) we notice two areas of combustion as a function of the pressure uniting for a corresponding pressure value at the lower limit of self-maintaining combustion of perchlorate alone. This is, for example, the case in the combustion of perchlorate in asymmetric dimethylhydrazine (Figure 8) studied by NADAUD [22].

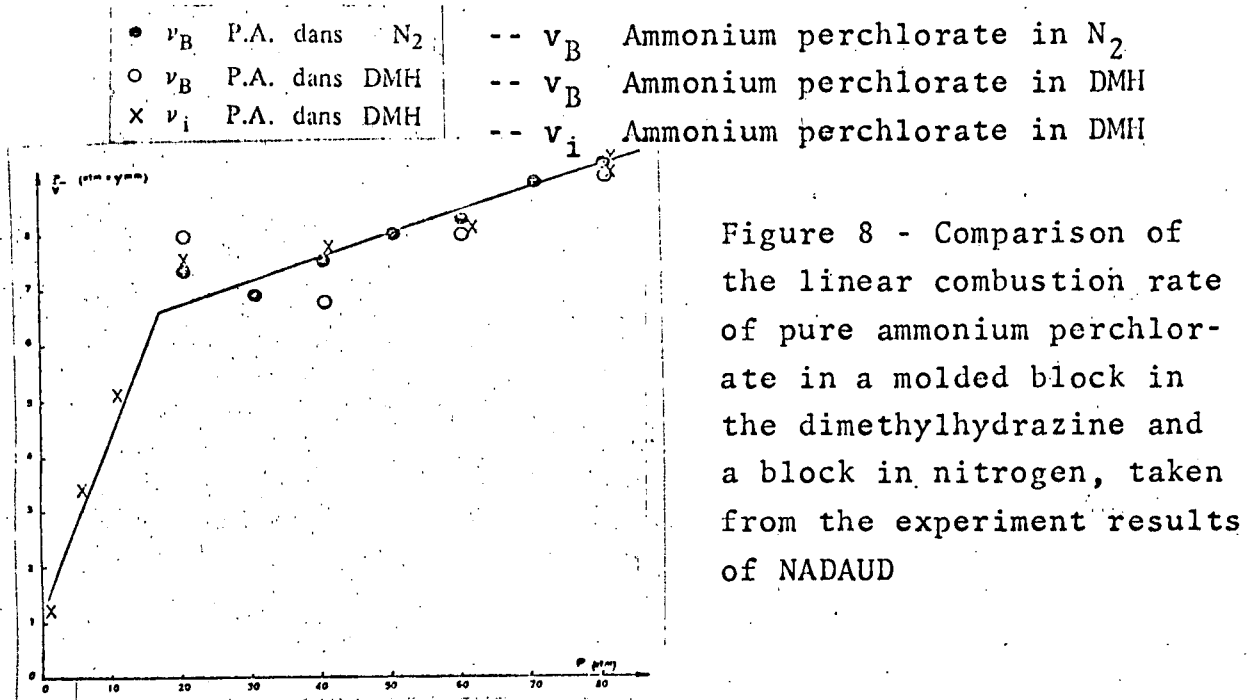


Figure 8 - Comparison of the linear combustion rate of pure ammonium perchlorate in a molded block in the dimethylhydrazine and a block in nitrogen, taken from the experiment results of NADAUD

3. INFLUENCE OF COMPOSITION PARAMETERS ON THE COMBUSTION OF PROPERGOLS HAVING AN AMMONIUM PERCHLORATE BASE

3.1. Influence of Perchlorate Particle Size Distribution

The case of perchlorate can be distinguished only from the case of powder.

3.1.1. In the first case, making $k=1/2$, the equation (8) is reduced to $\frac{P}{v_B} = \frac{1}{v_B^*(\phi)}$ ($2P^* = P$) when ϕ varies, the transformed allow a focal point on the axis of the P's at an abscissis

point $-2P^*$ or $\frac{2k_d}{k_a}$. This is what the properly extrapolated results of SCHANNON and PETERSEN [21] show (Figure 4). The study of the slope of the transformed as a function of the ψ allows making evident a law of the form $v_B^*(\phi) \propto \frac{1}{\alpha\phi + \beta}$ already noted [23].

3.1.2. In the second case, the equation may be written:

$$\frac{P}{v_B} = \frac{P^*}{v_B^*(X, \phi)} \left(2 + \frac{1 - X \frac{M_{PA}}{M_F}}{X \frac{M_{PA}}{M_F}} k + \frac{P}{P^*} \right) \quad (12)$$

It is observed that this equation differs from the preceding one (in addition to the terms of activation included in v_B^* and the terms of adsorption included in P^*) by the expression $\left[\frac{1 - X \frac{M_{PA}}{M_F}}{X \frac{M_{PA}}{M_F}} k \right]$ which introduces the fuel (percentage, molar mass, characteristics of pyrolysis). The analysis of the experiment results of BECKSTEAD [24] BACKHMAN [25] and TABACK [4] (Figures 9, 10, and 11) show that the transformed

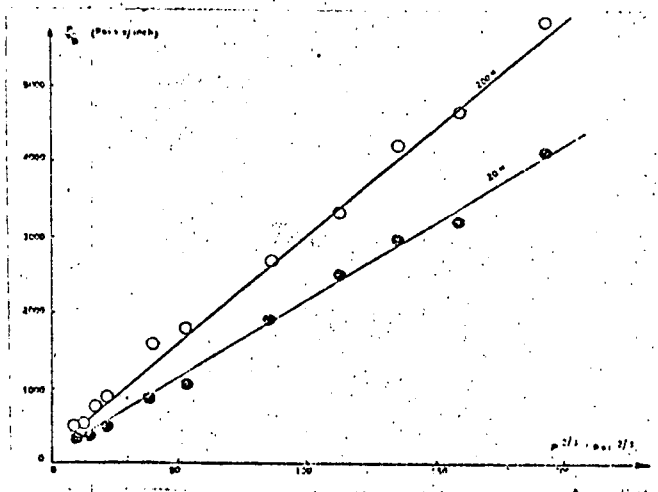


Figure 9 - Combustion of a propellant having an ammonium perchlorate base (binding agent polysulphur) for two different grain sizes, taken from the results of BECKSTEAD (ref No. 24).

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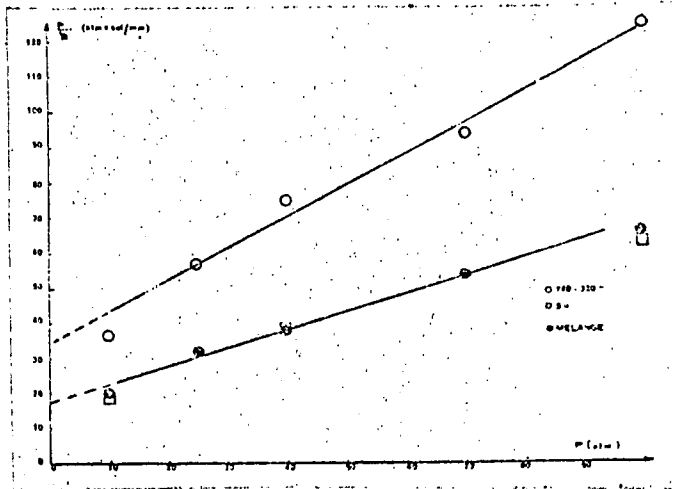


Figure 10 - Combustion of an ammonium perchlorate base propergol (binding agent: plexiglas) for different size grains (molar ratio $\alpha=2$) taken from the results of BACKHMAN (ref. No 25).

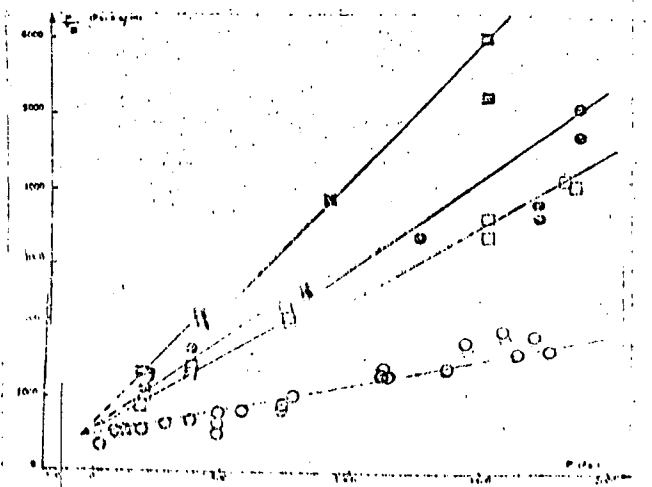


Figure 11 - Combustion of an ammonium perchlorate base propergol (binding agent: polyester) taken from the results of TABACK (ref. No. 4).

$\frac{P}{v_B}$: P are cut at one point which can be outside the axis of P.

Or C, the ordinate of the point. The empirical equation of this group of straight lines can be written:

$$\frac{P}{v_B} = \frac{1}{a'(X, \phi)} (2 + Ca'(X, \phi) + b'P) \quad (13)$$

or better in the form:

$$\left(\frac{P}{v_B} - C \right) = \frac{1}{a'(X, \phi)} (2 + b'P) \quad (13)$$

By bringing these equations closer to the equation (13) we see that they have the same form in relation to ϕ , to the condition of admitting that \underline{k} is proportional to the function $\underline{a'}$ (ϕ) which defines the reaction surface. Thus, in order to justify the empirical form of the laws of combustion rate for perchlorate associated with a combustible binding agent, we are lead to think that the number \underline{k} of small gaseous molecules given by a polymer molecule is proportional to the reaction surface which suggests a pyrolysis catalyzed by the surface.

Note that this phenomenon is best suggested by a different presentation of the equation (13) which can also be written:

$$v_B = \frac{\frac{a'(\phi)}{1 + Ca'(\phi)} P}{1 + \frac{b}{1 + Ca'(\phi)} P}$$

The term $1/1 + Ca'(\phi)$ is found to be a reducing coefficient of the partial pressure of the active agent (perchloric acid) even greater when the size of the grains is small. In the case where $C = 0$ ($k = 0$, absence of fuel) we arrive obviously at the simple equation:

$$v_B = \frac{a(\phi) P}{1 + b P}$$

3.2. Influence of the Concentration (1-X) of binding agent

The influence of the concentration of binding agent can be studied from the general equation (8) when X varies, the transformed must be displaced parallel to themselves since

only the ordinates at the origin of the formula $\frac{P^*}{v_B^*} K(X)$ is a function of X . This is what can be observed from the results of PITTMAN [15] (Figure 12) and those of BACKHMAN [25] (Figure 13). It can be written explicitly in relation to X :

$$\frac{1}{v_B} = \frac{1}{v_B^*} \left\{ \frac{P^*}{P} \left(2 - \frac{M_{PA}}{M_F} k \right) + 1 + \frac{P^*}{P} \frac{M_{PA}}{M_F} k \frac{1}{X} \right\}$$

Or, by appropriately regrouping the terms:

$$\frac{1}{v_B} - \frac{1}{v_B^*} \left(\frac{2P^*}{P} + 1 \right) = k \frac{M_{PA}}{M_F} \frac{P^*}{P} \left(\frac{1}{X} - 1 \right) \quad (14)$$

Thus, $\frac{1}{v_B}$ must be a linear function of $\frac{1}{X}$.

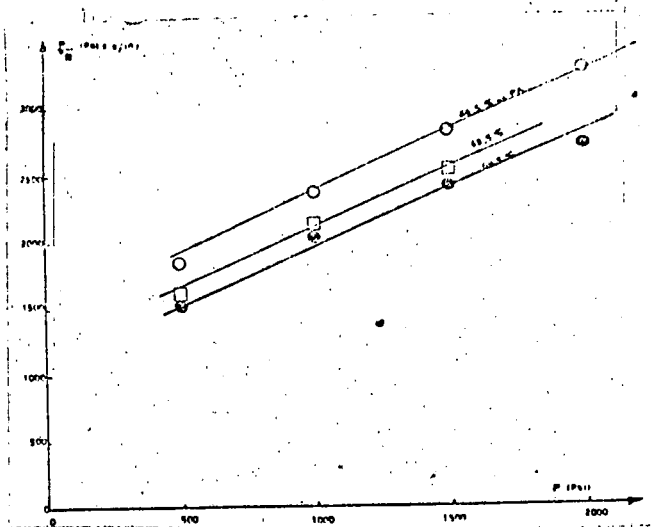


Figure 12 - Combustion of an ammonium perchlorate base propergol (binding agent polybutadene) for various proportions of ammonium perchlorate, taken from the results of PITTMAN (ref. No. 15)

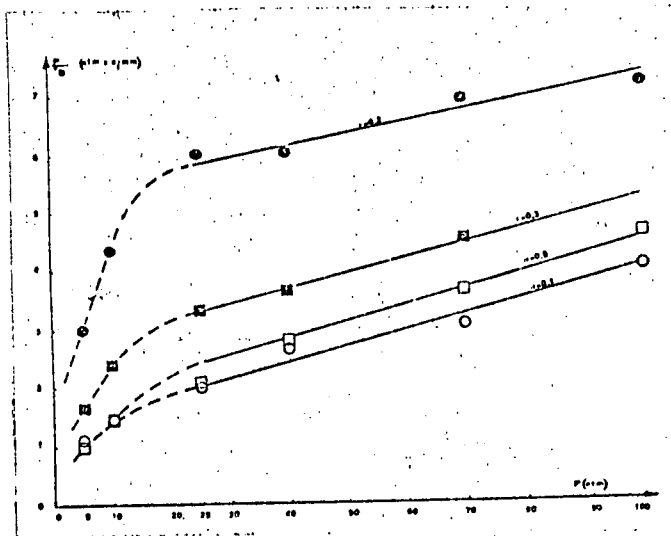


Figure 13 - Combustion of an ammonium perchlorate base propergol (binding agent: polystyrene) for different proportions of ammonium perchlorate, taken from the results of BACKHMAN (ref. No. 25).

This is verified from the results of PITTMAN [15] (Figure 14, figure without catalysts), at $P=Cte$. Thus the influence of the binding agent on the ammonium perchlorate combustion can be summarized in the following manner: On one hand, the presence of the binding agent can lead to the existence of a more rapid superficial reaction than in its absence, increasing the ablation speed in relation to that of pure ammonium perchlorate under the same conditions. On the other hand the effect of dilution of the binding agent pyrolyzed vapor in the presence of that of the active oxidizer responsible for this superficial reaction brings about a reduction of this speed, even more when the binding agent concentration in the propergol is higher.

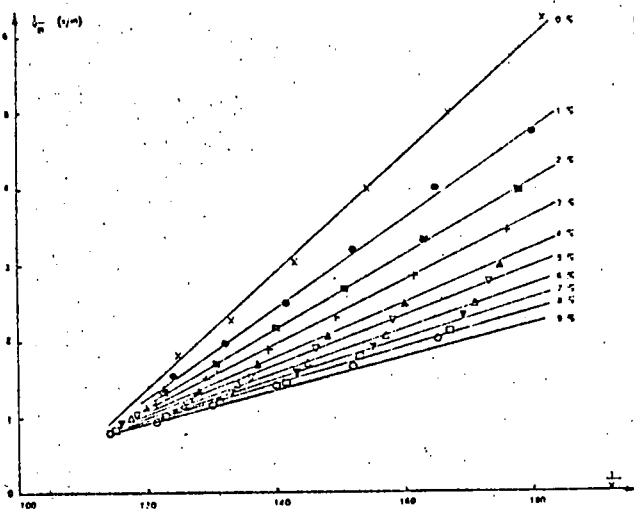


Figure 14 - Combustion of an ammonium perchlorate base propergol (binding agent: polyester). Influence of the catalyst rate, taken from the experiments of TABACK (ref. No. 4).

3.3. Influence of the Catalyst

The influence of the catalyst can be studied either as a function of the combustion pressure (at a constant composition of powder) or as a function of the binding agent content (at a constant pressure).

3.3.1. The study as a function of the pressure can be made from the general equation (12).

A priori, the catalyst can act on all the kinetic characteristics of the reaction: k_a/k_d (by P^*), k'_s (by v_B^*) and \underline{k} . The study of the influence of the copper chromite on the combustion of a propergol having an ammonium perchlorate base was done by TABACK [4] (Figure 15). We observed that when the concentration of chromite varies, the transformed show a focal point corresponding to a negative pressure. These results are brought closer to those of the same author concerning the influence of grain-size distribution of the

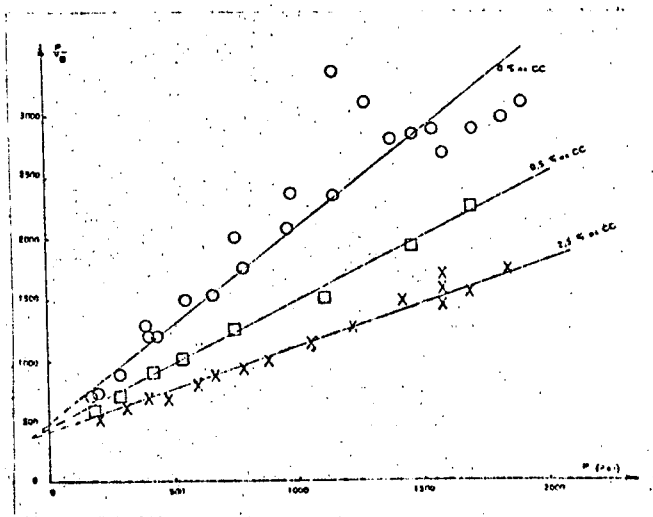


Figure 15 - Combustion of an ammonium perchlorate base propergol (binding agent polybutadene). Influence of the perchlorate rate and catalyst rate, taken from the experiments of PITTMAN (ref. No. 15).

perchlorate (Figure 11). Also, we observed that the coordinates of the focal point are the same in both cases.

We saw that the empirical equation of the transformed of the rate, as a function of the pressure, could be written according to the equation (13). The coordinates of the focal point being the same in the representations $P/v_B = f(P, \phi)$ and $P/v_B = f(P, \tau \text{ catalyst})$, we are lead to seek which factors impose this resemblance in the theory that we have proposed. The comparison of the empirical equation (13) with the general equation (12) allows writing for identification:

$$b' = \frac{1}{2P^*} \quad a'(\phi) = \frac{v_B^*(X, \phi)}{P^*}$$

$$C = \frac{1-X}{X} \frac{M_{PA}}{M_F} \frac{k(X, \phi)}{v_B^*(X, \phi)} P^*$$

Let us note immediately that the existence of a focal point when τ varies, compels C to be independent from ϕ , therefore too that $k(\phi)$ and $v_B^*(\phi)$ have the same form as $S(\phi)$.

The superposition of focal points allow writing:

$$(P^*) \tau_{\text{catalyst}} = (P^*) \phi, \text{ or: } \left(\frac{k(X, \phi)}{v_B^*(X, \phi)} \right) \tau_{\text{catalyst}} = \left(\frac{k(X, \phi)}{v_B^*(X, \phi)} \right) \phi$$

The results are that the catalyst does not affect the adsorption energy. Besides, as it is very highly unlikely that the diameter of the perchlorate grains play a role in the rate constant of the surface reaction, included in $v_B^*(X, \phi)$, we are lead to think that ϕ and τ_{catalyst} influence solely on the function $S(\phi)$ which defines the reaction surface. Thus ϕ could act on the apparent reaction surface, τ_{catalyst} on the number of active sites per surface unit.

3.3.2. The study as a function of the binding agent content which can be made from the equation (14) the terms which can be affected by the presence of the catalyst are again v_B^* , P^* , and k . In fact the analysis of the results of PITTMAN [15] (Figure 14) according to the representative $\frac{1}{v_B}$, $\frac{1}{X}$, allows making evident a focal point when $\frac{1}{X}$ varies. As a function of the statements made in paragraph 3.3.1. it would thus seem that the catalysts act only on k , by increasing there, even the number of pyrolitic sites available on the reaction surface. Nevertheless the abscissa of the focal point is not located exactly for $1/X = 1$, but for $1/X$ near 1.1, whereby X is near 0.88.

Two causes can be advanced in order to account for this variation in the theoretical law:

- The ordinate originating from the focal point is equal to

$\left[\frac{1}{v_B} \left(\frac{2P^*}{P} + 1 \right) \right]$ can be slightly noticeable when the catalyst is

present and provokes a focal point "drift".

- We can equally assume that a certain mass fraction of the binding agent, equal here to 0.12 would be necessary in order to carry out the proposed method of combustion. This value is moreover completely compatible with the porosity of the perchlorate grains, thus defining a mix limit ratio.

4 - DISCUSSION AND CONCLUSION

4.1. The theory demonstrated above permits us to account for the great majority of rate laws in terms of pressure, observed in practice. In fact the equation (6) for weak pressures is reduced to a linear equation (1) BARRERE law. For average pressures, we can assimilate the homographic form with the parabolic form given by the FREUNDLICH isotherme in expression of rate in the critical stage. Finally at high pressure, the existence of a plateau is shown by the general equation (7) in which we made $\alpha = \beta = 0$.

4.2. The values of α and β observed in practice are generally weak, and their precise determination, for each type, is taken from numerical calculation methods. At any rate, in a rather great number of cases, the experimental results which were given to us to analyze are linearized satisfactorily in one or the other of the representations P/v_B , P and P/v_B , $P^{2/3}$. We also saw that the first representation made the existence of

distinct kinetic operations more evident than the second.

4.3. In the experiments on free combustion of propergols with ammonium perchlorate base and combustible binding agent we observed that the results often satisfy the linear representation P/v_B , P causing as a result $\alpha = \beta = 0$. The phenomenon can have two causes:

- The area of pressure studied is small. The equilibrium of perchlorate dissociation brings into this area only a small temperature variation. The superficial reaction occurs then only in semi-isothermic conditions.

- A new monovariant equilibrium takes the place of the dissociative equilibrium of the perchlorate, introducing the very lowest temperature variations in the area of pressure studied. This is the case which can occur if the ammonia perchlorate dissolves in the combustion surface, or if certain additives (flux, for example) are used in the propergol.

4.4. The theory could be satisfactorily tested by including the perchlorate grain-size distribution, the binding agent concentration, and a catalyst. It has allowed defining more precisely the function of the copper chromite which would act on the binding agent's heterogenous pyrolysis.

4.5. Other aspects could be approached using this theory such as:

- the self-maintained combustion limit of perchlorate

- the effect of the initial temperature on the combustion rate

- the erosive combustion.

Resulting from this general report, they will be the subject of articles in specialized journals.

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